Folding kinetics of a single semiflexible polymer(Soft Matter as Structured Materials)

AUTHOR(S):

Yoshinaga, Natsuhiko

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Department of Physics, Kyoto University Natsuhiko Yoshinaga [1]

平衡状態における一分子の高分子鎖の構造はこれまで数多く議論されてきている。一方で、平衡から遠く離れた所での高分子鎖の振舞いは、重要な問題であるにもかかわらずあまり議論されていない。そこで、本研究では、単一セミフレキシブル高分子鎖の折り畳み過程の速度論について考察する。単一セミフレキシブル高分子鎖は、良溶媒から貧溶媒環境への変化に伴い、核形成・成長過程により折り畳まれる。一方、再び良溶媒環境に戻すと、今度は徐々にほどけていく過程が見られる。(Fig. 1) 本研究では、自由エネルギー変化と散逸のバランスからマクロな変数に対する運動方程式を求め、凝縮過程については核形成時間とその成長速度を、脱凝縮過程については鎖の広がりの動的スケーリング指数について議論する。

Compared to the understandings of equilibrium state, little is known about polymers far from equilibrium. Recently the kinetic aspects of single polymer molecules have become experimentally tractable and therefore theoretical studies are desired. Although the kinetics of ordering are a well-known problem and several investigations have already performed on flexible polymers, the kinetics of semiflexible polymers are less well understood.

Semiflexible polymers have been discussed as a simple model of biomacromolecules such as DNA and actin. Recent experiments and simulations have clarified that a single semiflexible polymer exhibits a first-order phase transition between elongated coil and folded compact states with a decrease in the solvent quality.[1] There, a single semiflexible polymer folds into various kinds of ordered structures such as a toroid or a rod, depending on its stiffness and temperature.

In this presentation, we theoretically discuss the transition kinetics of a single semiflexible polymer. Simulations have revealed that folding and unfolding transition can be divided into several characteristic regimes.[2] While the folding transition consists of the nucleation and growth process (Fig. 1A-D), the unfolding transition can be regarded as the three-step process. First a folded chain swells (Fig. 1E, F), then gradually increases its size (Fig. 1F, G), and finally relaxes into the coiled state (Fig. 1G, H). The origin of the appearance of the second stage is the fact that although the volume energy is almost lost during the first stage, the chain cannot elongate rapidly after that due to entanglements.

[1]E-mail: yoshinaga@scphys.kyoto-u.ac.jp

We can consider the balance between the free energy change and dissipative heat.[3] The dissipative heat is exhausted by the entropy production of solvent molecules, and therefore,

$$\frac{\mathrm{d}F}{\mathrm{d}t} = -T\frac{\mathrm{d}S}{\mathrm{d}t}, \tag{1}$$

is satisfied. Calculation of the free energy and the dissipation (hydrodynamic and frictional dissipation) leads to the equation of motion of coarse-grained valuables.

In the folding process, we can calculate the nucleation time τ, and for the small persistence length, it exponentially increases as the larger persistence length;

$$\tau \sim \eta \exp\left[\frac{\mu l_p}{\epsilon}\right], \tag{2}$$

where μ, l_p and ϵ are surface tension of a collapsed polymer, the persistence length and the coupling constant of attractive interactions, respectively. For the large persistence length, the dependence becomes rather gentle since the friction is effectively small. The growth rate can also be calculated and as a result it is found that the nucleus evolves linear in time.

On the other hand, in the unfolding process, the size of a chain R evolves as

$$R \sim \begin{cases} t^{1/8} & \text{for disentanglement,} \\ t^{1/4} & \text{for relaxation.} \end{cases} \tag{3}$$

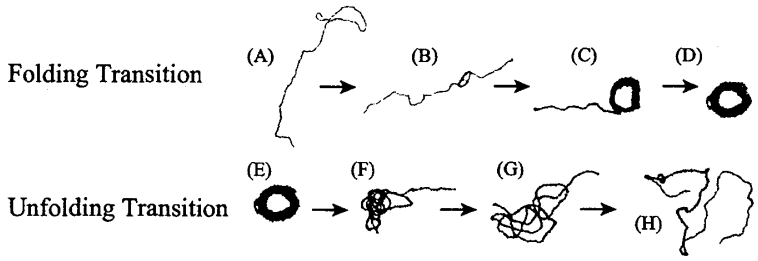

Figure 1: Typical snapshots of a single semiflexible polymer in the process of the folding and unfolding transition.

References

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